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Solving the Schrödinger equation for helium atom and its isoelectronic ions with the free iterative complement interaction (ICI) method

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The Schrödinger equation was solved very accurately for helium atom and its isoelectronic ions ($Z=1-10$) with the free iterative complement interaction (ICI) method followed by the variational principle. We obtained highly accurate wave functions and energies of helium atom and its isoelectronic ions. For helium, the calculated energy was **-2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37** a.u., correct over 40 digit accuracy, and for H^- , it was **-0.527 751 016 544 377 196 590 814 566 747 511** 383 045 02 a.u. These results prove numerically that with the free ICI method, we can calculate the solutions of the Schrödinger equation as accurately as one desires. We examined several types of scaling function g and initial function ψ_0 of the free ICI method. The performance was good when logarithm functions were used in the initial function because the logarithm function is physically essential for three-particle collision area. The best performance was obtained when we introduce a new logarithm function containing not only r_1 and r_2 but also r_{12} in the same logarithm function. © 2007 American Institute of Physics. [DOI: 10.1063/1.2801981]

I. INTRODUCTION

As Dirac noted, the Schrödinger equation (SE) describes accurately the electronic structures of atomic and molecular systems.¹ Hydrogen atom was a brilliant example of the accurate nature of the SE. Next was helium atom and therefore immediately after the SE was born, Hylleraas² applied it to helium atom and published a very important result, which was very accurate, though it was still far from exact. Since then, many people tried to accurately solve the SE of helium atom,²⁻¹⁵ since solving the SE of helium atom might give us a simple but important insight in formulating the exact solutions of the SE for more general systems. This stream of studies may be called an explicitly correlated wave function theory.

Hylleraas considered intuitively that the wave function of helium atom should be expressed to a good approximation as

$$\sum c_{(l,m,n)} s^l t^m u^n \exp(-\alpha s), \quad (1)$$

where $\{s, t, u\}$ is a coordinate system defined by

$$\begin{aligned} s &= r_1 + r_2, \\ t &= r_1 - r_2, \end{aligned} \quad (2)$$

$$u = r_{12},$$

which is valid for the S state of helium atom. $\{l, m, n\}$ is a set of integers and $c_{(l,m,n)}$ is a coefficient to be determined by variational principle. This expansion of the wave function

was called Hylleraas expansion. He introduced interelectron distance u ($=r_{12}$) explicitly in the wave function, which was an origin of his remarkably good result in contrast to the results of the orbital-based theory. After Hylleraas's pioneering work, the analytical wave functions including r_{12} explicitly in many different ways have been studied.³⁻¹⁷ Table I is a brief summary of the history of accurate calculations of the ground state of helium atom.

In the original Hylleraas expansion, the integer set was limited to be all non-negative. Kinoshita⁶ found that, when $\{l, n\}$ in Eq. (1) were permitted to be negative, significantly improved results could be obtained. Thakkar and Koga⁸ extended even to half-integers and obtained quite excellent results.

Bartlett, Jr.,³ Gronwall,⁴ Fock,⁵ and others^{7,18} clarified some insufficiency in the Hylleraas function as compared to the exact wave function. They argued that the Hylleraas function was adequate for the description of two-particle cusp conditions¹⁶ but insufficient for the three-particle coalescence region. They suggested that including logarithm singularity in the wave function would be important for this region. Frankowski and Pekeris⁷ performed numerical calculations using such logarithm function and showed a remarkable performance. Their wave function is expressed as

$$\sum c_{(l,m,n,i,j)} s^l t^m u^n (s^2 + t^2)^{i/2} (\ln s)^j \exp(-\alpha s), \quad (3)$$

where l runs all integers and $\{m, n\}$, $\{i, j\}$ are non-negative integers. The original logarithm form suggested by Bartlett, Gronwall, and Fock contained the $(\ln[(s^2 + t^2)^{1/2}])^j$ term,³⁻⁵ but they modified it to simpler $\ln s$ form for numerically stable calculations. Then, the ground-state energy of the he-

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TABLE I. History of the accurate calculations of the ground state of helium atom.

Year	Ref.	Type	Energy (a.u.)
1929	Hylleraas (Ref. 2)	Hylleraas (three terms)	−2.902 43
1957	Kinoshita (Ref. 6)	Kinoshita type	−2.903 722 5
1966	Frankowski and Pekeris (Ref. 7)	Logarithm	−2.903 724 377 032 6
1994	Thakkar and Koga (Ref. 8)	Half-integer	−2.903 724 377 034 114 4
1998	Goldman (Ref. 9)	Polynomial	−2.903 724 377 034 119 594
1999	Drake (Ref. 10)	Double exponent	−2.903 724 377 034 119 596
2002	Sims and Hagstrom (Ref. 12)	Hylleraas-CI	−2.903 724 377 034 119 598 29 99
2002	Drake <i>et al.</i> (Ref. 11)	Triple exponent	−2.903 724 377 034 119 598 305
2002	Korobov (Ref. 13)	Slater geminal	−2.903 724 377 034 119 598 311 158 7
2006	Schwartz (Ref. 15)	Logarithm (ln(<i>s</i>))	−2.903 724 377 034 119 598 311 159 245 194 404 440 049 5
2007	This work	ICI (new logarithm)	−2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37

lium atom was greatly improved, reflecting the improvement in the three-particle coalescence region.

Recently, since computer technology has been much advanced, extensively high-level calculations have become possible. The calculations using a large number of orthogonal polynomial basis functions were reported by Goldman.⁹ Drake *et al.*^{10,11} performed calculations with double and triple exponent basis functions. Sims and Hagstrom¹² reported Hylleraas-configuration interaction (CI) results with a large number of basis functions. Korobov¹³ performed extensive calculations using a very large number of Slater-type geminal functions and optimizing their nonlinear exponent parameters, the energy accurate to 25 digits was obtained. In particular, recently, Schwartz¹⁵ systematically performed computational experiments using several sets of basis functions including logarithm functions and obtained the energy correct up to 36 figures! His wave function is slightly different from that of Frankowski and Pekeris and expressed as

$$\sum c_{(l,m,n,j)} s^l (t/s)^m (u/s)^n (\ln s)^j \exp(-\alpha s), \quad (4)$$

where j is 0 or 1 and $\{l, m, n\}$ run non-negative integers. This form was easier to calculate than that including the $(s^2 + t^2)$ term introduced by Frankowski and Pekeris. The negative-integer powers of s are also different from those of Kinoshita, which was $(t/u)^m$ instead of $(t/s)^m$. His idea was different from Kinoshita's original one and led to an easier calculation. Schwartz had been able to obtain a surprisingly accurate result, which was certainly a milestone in the history of solving the SE of atoms and molecules. Actually, his study has become a very good reference in our present study.

Making a bird's-eye view of the history of solving the SE of helium atom, we noticed that a critical advancement was made when basic physical insight was realized in the calculations. Though these intuitions were incredibly valuable, it was difficult to generalize them for solving the SE of general atoms and molecules. The SE was believed not to be soluble for more than 80 years since its birth, and there was no general theory leading to the exact solution of the SE.

Recently, we have formulated a general theory of solving the SE of atoms and molecules.^{19–25} We started from analyzing the structure of the exact wave function and proposed the iterative complement (or configuration) interaction (ICI)

method that is guaranteed to converge to the exact wave function.¹⁹ The singularity difficulty that is the problem caused by the divergence of the integrals of higher powers of Hamiltonian was solved by introducing the scaled Schrödinger equation (SSE).²⁰ The free ICI method²⁰ was also introduced at the same time. It is a flexible method and is more rapidly converging than the original ICI method. We will briefly explain the free ICI method in the next section. We note that the ICI methodology is useful not only for solving the nonrelativistic SE (Refs. 21–23 and 25) but also for solving the relativistic Dirac-Coulomb equation²⁴ of atoms and molecules.

The purpose of this article is to give benchmark calculations of helium and its isoelectronic atoms to see how accurately the free ICI method works for solving the SE. Because of the existence of the accumulated history of the accurate calculations of helium atom as overviewed above, we can formulate our free ICI calculations effectively and examine the accuracy of our results in great detail.

Our basic Hamiltonian is a fixed-nucleus Born-Oppenheimer one, so that the corresponding energy correct up to 36 decimal figures may be unnecessary because other physical effects such as nuclear motion, relativistic effect, fine and hyperfine structural effects, etc., are more important than these decimal figures of the energy. The test we want to pursue in this paper is how accurately and effectively the free ICI method solves the SE whose Hamiltonian is fixed, in this case, to the Born-Oppenheimer nonrelativistic one. When we modify our basic Hamiltonian to include other effects, the free ICI method will give the solution corresponding to that Hamiltonian. In the free ICI methodology, the Hamiltonian paves his own way to generate his own wave function. Of course, we may use the present wave function as an accurate zeroth order wave function when we deal with these effects by perturbation method.

II. FORMULATION

We want to solve the SE for the ground state of helium and its isoelectronic atoms by using the free ICI method. The nucleus is treated as fixed at the origin of the coordinate and we consider the motions of two electrons attracted by the

Coulomb forces from the nucleus. The ground state of the helium atom has a zero spatial angular momentum, i.e., S state. Therefore, only interparticle coordinates $\{r_1, r_2, r_{12}\}$ are enough to describe the wave function for the ground state. The Hamiltonian for the states of S symmetry in the $\{r_1, r_2, r_{12}\}$ coordinates is written as

$$H = -\frac{1}{2} \sum_{i=1}^2 \left(\frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} \right) - \left(\frac{\partial^2}{\partial r_{12}^2} + \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} \right) - \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_2^2 + r_{12}^2 - r_1^2}{2r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} - \sum_{i=1}^2 \frac{Z}{r_i} + \frac{1}{r_{12}}. \quad (5)$$

The volume element of this coordinate is $8\pi^2 r_1 r_2 r_{12}$. We also adopted the $\{s, t, u\}$ coordinate system defined by Eq. (2) originally used by Hylleraas, whose volume element is $8\pi^2 (s^2 - t^2)u$. The Hamiltonian in this coordinate is written as

$$H = - \left(\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{\partial^2}{\partial u^2} \right) - 2 \frac{s(u^2 - t^2)}{u(s^2 - t^2)} \frac{\partial^2}{\partial s \partial u} - 2 \frac{t(s^2 - u^2)}{u(s^2 - t^2)} \frac{\partial^2}{\partial u \partial t} - \frac{4s}{s^2 - t^2} \frac{\partial}{\partial s} - \frac{2}{u} \frac{\partial}{\partial u} + \frac{4t}{s^2 - t^2} \frac{\partial}{\partial t} - \frac{4sZ}{s^2 - t^2} + \frac{1}{u}. \quad (6)$$

In Eqs. (5) and (6), the Coulomb potential is

$$V = V_{Ne} + V_{ee} = - \sum_{i=1}^2 \frac{Z}{r_i} + \frac{1}{r_{12}} = - \frac{4sZ}{s^2 - t^2} + \frac{1}{u}, \quad (7)$$

where V_{Ne} and V_{ee} represent the nuclear attraction potential and electron repulsion term, respectively, and Z is the nuclear charge. The other terms in Eqs. (5) and (6) are from the kinetic operator.

Next, we briefly explain the ICI methodology.¹⁹⁻²¹ As seen from Eq. (7), the Hamiltonian of atoms and molecules includes Coulomb singularities at two-particle coalescence. For this singularity, the integrals of higher powers of Hamiltonian diverge.²⁰ The ICI theory based on the normal SE includes such higher powers of the Hamiltonian, and therefore has a difficulty. To avoid such difficulty, we introduced the SSE given by²⁰

$$g(H - E)\psi = 0, \quad (8)$$

where g is a scaling function that is totally symmetric and positive everywhere except at the singular points r_0 , but even there, it should satisfy

$$\lim_{r \rightarrow r_0} gV = a, \quad (9)$$

with a being a nonzero constant to not eliminate the information of the Hamiltonian at the singular points. The ICI wave function based on the SSE is defined by

$$\psi_{n+1} = [1 + C_n g(H - E_n)]\psi_n, \quad (10)$$

which is guaranteed to converge to the exact solution as

iteration proceeds without encountering the singularity problem for the existence of the g function. The above function includes only one variational parameter C_n for each iteration cycle, so we call it the simplest ICI (SICI) wave function.

We introduce here the free ICI method.²⁰ We collect all linearly independent functions $\{\phi_i^{(n)}\}$, $i=1, 2, \dots, M_n$ from the right-hand side of Eq. (10) and give an independent coefficient to each as

$$\psi_n = \sum_{i=1}^{M_n} c_i^{(n)} \phi_i^{(n)}. \quad (11)$$

In the above formulation, all the functions $\{\phi_i^{(n)}\}$ were generated by the SICI operators of Eq. (10) and assigned free variational coefficients, so that the free ICI converges faster than the original SICI. In the present calculations, the coefficients $\{c_i^{(n)}\}$ are determined with the variational principle. In the free ICI method, the calculations at $n+1$ do not refer to the coefficients $\{c_i^{(n)}\}$ at n , so that we may call n as *order* instead of *iteration number*.

The exact electronic wave function must satisfy the antisymmetric condition and spin and spatial symmetries. When we start from some initial function ψ_0 that satisfies these symmetry conditions, the ICI and free ICI methods retain their symmetry throughout the calculations since the Hamiltonian and g function are totally symmetric. For the present two-electron atoms, the spatial and spin parts are completely separable. Since the ground state of helium atom is singlet, the spatial part must be symmetric to the permutation of two electrons.

III. DETAILS OF CALCULATIONS

In the free ICI method, we have two freedoms: one is the g function and the other is the initial function ψ_0 . We have examined several sets of g and ψ_0 to investigate the nature of the functions the free ICI method generates and the convergent behavior to the exact solution.

First, let us discuss on the choice of the g function. Since the role of the g function is to eliminate the singularities due to the Coulomb potential, it should have an inverse order of the Coulomb potential at the singular points. So, the first choice may be

$$g = \frac{1}{V_{ee} - V_{Ne}}, \quad (12)$$

where the sign of V_{Ne} was inverted to make the g function positive everywhere except at the singular points. However, this g function generates complicated functions and the integrations may become difficult.

In the next choice, we first separate V into V_{Ne} and V_{ee} , take the inverse of each, and then take a product or a sum as

$$g_P^1 = \frac{1}{V_{Ne}} \frac{1}{V_{ee}}, \quad (13)$$

$$g_s^1 = -\frac{1}{V_{Ne}} + \frac{1}{V_{ee}}. \quad (14)$$

The sum formula g_s^1 generates more flexible complement functions than the product formula g_p^1 since the product formula g_p^1 does not strictly satisfy the condition of Eq. (9) for the individual singular point (a can become zero). We have further examined the following g function:

$$g_s^{1+} = 1 - \frac{1}{V_{Ne}} + \frac{1}{V_{ee}}, \quad (15)$$

which includes a nonscaling factor of unity. Since generally the Hamiltonian includes singular and nonsingular parts, it is recommended to take the form of Eq. (15) rather than that of Eq. (14). When we include unity in the g function, the free ICI generates not only regular but also singular functions as bases for the wave function, but the singular one must be eliminated since the wave function must be integrable finite. When we did so, we found that both Eqs. (14) and (15) give almost the same results in the present calculations and, therefore, we did not use Eq. (15) in the present nonrelativistic calculations. However, we note that the unity in the g function is important for solving the relativistic Dirac-Coulomb equation because this term works to keep the balancing condition (ICI balance) between the large and small components.²⁴

Another simple choice in the line of the argument above would be

$$g_p^2 = r_1 r_2 r_{12}, \quad (16)$$

$$g_s^2 = r_1 + r_2 + r_{12}, \quad (17)$$

$$g_s^{2+} = 1 + r_1 + r_2 + r_{12}. \quad (18)$$

Again, the product form g_p^2 is not recommended because it does not strictly satisfy the requirement given by Eq. (9). The unity in Eq. (18) was also not important and so we did not use Eq. (18). When these g functions are used, the generated complement functions generally have a simpler form than those obtained using Eqs. (14) and (15), so that this choice would be suitable for many-electron systems. However, in the $\{s, t, u\}$ coordinate system of the helium atom, the generated functions using Eqs. (13)–(15) are also simple and do not cause any difficulty at all. In the next section, we will see the different performance of the g functions given above.

Next is the choice of the initial function ψ_0 , which is very important since the functional form of the ICI complement functions is mostly determined by that of ψ_0 . We can generally expect that the ψ_0 chosen cleverly on the physical grounds shows good performance in convergence.²⁵ For helium, the simplest choice of ψ_0 would be a product of the atomic orbitals of two electrons,

$$\psi_0^{\text{nor}} = \exp[-\alpha(r_1 + r_2)] = \exp(-\alpha s). \quad (19)$$

We call this initial function “normal type.” The orbital exponent α may be treated as a nonlinear variational parameter, though this is not strictly necessary. The variational ground-state energy for this initial function is well known to be

$-2.847\,656\,245$ a.u., and the optimized α is $27/16=1.6875$.

Let us consider some necessary conditions that the exact wave function must satisfy. A major concern would be nuclear-electron and electron-electron cusp conditions since the electronic structure near the nucleus sensitively affects the energy of the atom. Though these properties are already taken into account in Eq. (19) in a variational sense as the iteration proceeds, we may introduce a more flexible form. A choice would be half-integer functions of s and u . When we do not include a half-integer at the beginning in ψ_0 , such functions are never generated in the ICI formalism. If such types of functions are important, they are expressed in the free ICI formalism by the sum of the integer-type functions. For rapid convergence, it is clever to introduce such functions in the initial function. An inclusion of the half-integer functions, together with the integer ones, would obviously make the descriptions more flexible especially in the particle-coalescence region. Recently, Thakkar and Koga¹⁴ reported such calculations and even introduced the functions of real number powers of s and u coordinates, showing an excellent convergence. We examine here the following two “half-integer-type” initial functions:

$$\psi_0^{\text{half } 1} = (1 + s^{1/2})\exp(-\alpha s), \quad (20)$$

$$\psi_0^{\text{half } 2} = (1 + s^{1/2} + u^{1/2})\exp(-\alpha s). \quad (21)$$

As discussed by Bartlett, Gronwall, and Fock,³⁻⁵ the three-particle collision effects may become important for very high-precision calculations aimed in this study. This effect is brought about effectively with the logarithmic mild singularity. Among the several logarithm functions proposed,^{3-5,7,15} Frankowski and Pekeris⁷ introduced $\ln s$ as a numerically stable form. Schwartz¹⁵ also reported extensive numerical calculations using $\ln s$. So, we first use this logarithm function as

$$\psi_0^{\text{log } 1} = (1 + \ln s)\exp(-\alpha s). \quad (22)$$

In the three-particle collision area, all of the interparticle distances $\{r_1, r_2, r_{12}\}$ become 0. However, the above logarithm function does not explicitly contain the electron-electron distance $r_{12}=u$. Certainly, the Coulomb potential between electron and nucleus is attractive, while the electron-electron potential is repulsive, so that the coordinates, $\{r_1, r_2\}$ and r_{12} may have different effects. The logarithm functions related to $\{r_1, r_2\}$ had been suggested by several authors^{3-5,7,15} but there had been no calculations with the logarithm functions explicitly including r_{12} . In the present paper, we examine for the first time the logarithm functions containing the r_{12} coordinate. So, our second logarithm initial function includes $\ln u$ in addition to $\ln s$ as

$$\psi_0^{\text{log } 2} = (1 + \ln s + \ln u)\exp(-\alpha s). \quad (23)$$

However, unfortunately, this function has a very weak point of unsatisfying the electron-electron cusp condition. The $\ln u$ term diverges as u approaches 0, though the other integrals remain finite because the logarithm singularity is milder than $1/u$.

To improve this problem, we propose the following “new logarithm” function for the initial function:

$$\psi_0^{\text{new log}} = [1 + \ln(s + \beta u)] \exp(-\alpha s), \quad (24)$$

where the parameter β was introduced as another nonlinear parameter, reflecting the difference between the electron nuclear potential and the electron-electron potential. This function includes both $\{r_1, r_2\}$ and r_{12} in the same logarithm. In the Hamiltonian, the Coulomb potentials of all interparticle coordinates $\{r_1, r_2, r_{12}\}$ are proportional to $1/r$ in the same manner, so that these three distances should be treated in the same way in the logarithm functions, which suggests $\beta=1$. Further, when $\beta > -1$, this function never becomes singular at any configuration except for the three-particle collision point where $s=0$ and $u=0$. It never conflicts with the two-electron cusp condition. If necessary, we can make r_{12} scaled to be suitable for the system by the parameter β , but $\beta \neq 0$ since it leads to $\psi_0^{\log 1}$ with $\beta=0$.

We performed calculations with some combinations of g and ψ_0 . There, the functions having negative integers on the u coordinate were eliminated because they never satisfy the two-electron cusp condition. The analytical formulations for calculating the integrals over the complement functions are given in the Appendix, especially for the logarithm functions.

The calculations have been performed with our original program, which consists of three steps. In the first step, we generate the free ICI complement functions by using Eqs. (10) and (11) the second step creates the Hamiltonian and overlap matrices by doing analytical integrations over the complement functions, and the final step is the diagonalization. The first and second steps were formulated with the mathematical arithmetic software MAPLE.²⁶ For the final step, we formulated our own original eigenvalue solver for arbitrary precision with the GNU multiple precision²⁷ (GMP) arithmetic library. Since the calculations must be performed in very high accuracy, we used MAPLE and GMP with 120-decimal-figure accuracy for the calculations less than 10 000 dimensions and with 160-decimal-figure accuracy for more than 10 000 dimensions.

IV. RESULTS

A. Comparison of g functions with normal-type initial function

First, we examined the convergence behavior using different types of g functions combined with the simplest normal-type initial function given by Eq. (19). In the calculations with g_P^1 and g_S^1 , the $\{s, t, u\}$ coordinate was used and the free ICI wave functions generated have the common form as given by

$$\psi = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} \exp(-\alpha s), \quad (25)$$

where c_i is the variational parameter. For singlet state, m_i must be even integers. The integer sets $\{l_i, m_i, n_i\}$ are different for g_P^1 and g_S^1 . With g_S^1 , the complement functions with

negative powers of s are generated. l_i runs all integers while $\{m_i, n_i\}$ run non-negative integers. On the other hand, with g_P^1 , these negative powers were not generated. The importance of the negative powers of s was first shown by Kinoshita,⁶ who reported that, by inclusion of negative powers of s into the basis functions, the calculated energies were considerably improved. In the present ICI method, such functions are automatically generated if g_S^1 is used.

In the calculations with g_P^2 and g_S^2 , the $\{r_1, r_2, r_{12}\}$ coordinates were used. The free ICI wave functions are written commonly to g_P^2 and g_S^2 as

$$\psi = \sum_i c_i r_1^{l_i} r_2^{m_i} r_{12}^{n_i} \exp(-\alpha r_1) \exp(-\alpha r_2), \quad (26)$$

where $\{l_i, m_i, n_i\}$ run non-negative integers. The index sets of $\{l_i, m_i, n_i\}$ are also different for g_P^2 and g_S^2 .

Table II shows the calculated energies obtained with these four g functions at different iterations or orders n , M_n being the number of complement functions at n . The nonlinear parameter α was variationally optimized at each iteration and given in the table, where the value in parentheses is a guess optimal value, which was not strictly optimized. The calculations were stopped when M_n exceeds 1000. In all cases, the energy approaches the best value from above and the so-called chemical accuracy, i.e., millihartree accuracy, is achieved quite quickly already at the second iteration with $M_n=10-30$. With about $M_n=70$, the energies are correct to microharteers (six or seven decimal figures) except for g_P^2 . We can obtain chemical and spectroscopic accuracies in energy at a few iteration or order with the free ICI method.

Between the product-type and sum-type g functions, the latter gives slightly better convergent behavior. The complement functions with sum type contain all the complement functions with product type if n is large enough. As stated in Sec. III, the sum type is theoretically better than the product type. Comparing the energies with g_S^1 and g_S^2 (both are sum type), the former showed slightly better convergence than the latter, but the difference is small. For the present system, the $\{s, t, u\}$ coordinate is convenient to treat both differentiations and integrations and the symmetry of electron permutation is contained from their definition. So, we hereafter use the $\{s, t, u\}$ coordinate.

B. Comparison of the initial functions: Half-integer and logarithm types

Next we examine different initial functions using g_S^1 commonly in the $\{s, t, u\}$ coordinate. As shown above, the normal-type initial function ψ_0^{nor} showed good performance for getting chemical and even spectroscopic accuracies for any g function. The speed of convergence, however, became slow from beyond approximately ten-decimal-figure accuracy, indicating that the functions generated from ψ_0^{nor} alone could not efficiently describe the three-particle coalescence region, though with much iteration, such mild singularities should also be described. To overcome such problem, we

TABLE II. Ground-state energy of helium atom calculated with the different scaling functions g_P^1 , g_S^1 , g_P^2 , and g_S^2 given by Eqs. (13), (14), (16), and (17) combined with the normal-type initial function ψ_0^{nor} given by Eq. (19).

n^a	M_n^b	Optimal α	Energy (a.u.)	M_n^b	Optimal α	Energy (a.u.)
			g_P^1			
0	1	1.688	−2.847 656 245 00	1	1.688	−2.847 656 245 00
1	6	1.673	−2.901 577 012 47	4	1.846	−2.894 789 971 44
2	26	1.880	−2.903 708 675 01	19	2.096	−2.903 330 069 32
3	74	2.033	−2.903 723 900 61	49	2.189	−2.903 664 325 16
4	159	2.200	−2.903 724 347 07	105	2.233	−2.903 709 825 10
5	291	2.331	−2.903 724 372 74	185	2.258	−2.903 719 695 76
6	481	2.450	−2.903 724 376 36	304	2.279	−2.903 722 572 76
7	738	2.680	−2.903 724 376 83	457	2.294	−2.903 723 581 57
8	1074	2.753	−2.903 724 376 99	663	2.306	−2.903 723 990 22
9				913	2.315	−2.903 724 173 59
10				1229	2.321	−2.903 724 263 26
			g_S^1			
0	1	1.688	−2.847 656 250 00	1	1.687	−2.847 656 250 00
1	4	1.689	−2.901 337 956 94	3	1.813	−2.891 232 351 94
2	16	1.736	−2.903 642 984 26	7	1.814	−2.903 425 854 80
3	37	1.779	−2.903 720 264 20	13	1.906	−2.903 640 470 50
4	71	1.837	−2.903 724 018 70	22	2.038	−2.903 713 945 01
5	121	1.920	−2.903 724 323 45	34	2.113	−2.903 720 967 80
6	190	1.995	−2.903 724 364 00	50	2.236	−2.903 723 701 90
7	281	2.083	−2.903 724 373 59	70	2.309	−2.903 724 105 01
8	397	2.161	−2.903 724 375 90	95	2.427	−2.903 724 305 38
9	541	2.251	−2.903 724 376 66	125	2.503	−2.903 724 343 87
10	716	2.327	−2.903 724 376 88	161	2.615	−2.903 724 366 43
11	925	2.416	−2.903 724 376 97	203	2.689	−2.903 724 371 61
12	1171	2.495	−2.903 724 377 00	252	2.802	−2.903 724 375 03
13				308	2.861	−2.903 724 375 92
14				372	2.942	−2.903 724 376 56
15				444	3.058	−2.903 724 376 76
16				525	3.166	−2.903 724 376 91
17				615	3.239	−2.903 724 376 96
18				715	3.346	−2.903 724 376 99
19				825	3.416	−2.903 724 377 01
20				946	3.520	−2.903 724 377 02
21				1078	3.591	−2.903 724 377 02
Ref. 15			−2.903 724 377 03			
						−2.903 724 377 03

^aNumber of iteration or order.^bNumber of basis functions at order n .

may add in ψ_0 some functions that generate more flexible complement functions.

We examined then the initial functions including half-integer functions $\psi_0^{\text{half } 1}$ and $\psi_0^{\text{half } 2}$ of Eqs. (20) and (21). The free ICI wave functions generated from these initial functions are

$$\psi^{\text{half}} = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} \exp(-\alpha s), \quad (27)$$

where m_i runs even integers for singlet. From $\psi_0^{\text{half } 1}$, n_i is non-negative integers and l_i runs all integers and half-integers. From $\psi_0^{\text{half } 2}$, both l_i and n_i run integers and half-integers and n_i is non-negative. Table III shows the energies calculated from the half-integer-type initial functions. We stopped the calculations when M_n exceeded 4000. The convergent behavior to the exact solution was greatly improved over the case of ψ_0^{nor} shown in Table II. For example,

compared to the energy with g_S^1 at $n=12$ ($M_n=1171$) in Table II (−2.903 724 377 00 a.u., ten-decimal-figure accuracy), the energy with $\psi_0^{\text{half } 1}$ in Table III already exceeds this accuracy (−2.903 724 377 01 a.u.) at $n=6$ ($M_n=386$), and with $\psi_0^{\text{half } 2}$, the energy is −2.903 724 377 03 a.u. already at $n=4$ ($M_n=217$). The function $\psi_0^{\text{half } 2}$, showed better performance than $\psi_0^{\text{half } 1}$. The speed of convergence did not slow down even when exceeding $M_n=1000$, but it slowed down around $M_n=3000$ –4000. As shown by Thakkar and Koga,¹⁴ the functions with the powers of other fractional numbers and even of real numbers may greatly improve the convergence. These kinds of functions may be understood as introducing mild negative-power terms of s and u , like $s^{1/2} = s \cdot s^{-1/2}$, where the power of $s^{-1/2}$ is median between those of s^{-1} and $\ln s$ around $s=0$.

In contrast to the half-integer types, the logarithm function has a definite physics of adequately describing three-

TABLE III. Ground-state energy of helium atom calculated with the half-integer-type initial functions $\psi_0^{\text{half } 1}$ and $\psi_0^{\text{half } 2}$ given by Eqs. (20) and (21). The g function was commonly g_S given by Eq. (14).

n^a	M_n^b	Optimal α	Energy (a.u.)
$\psi_0^{\text{half } 1}$			
0	2	1.687	-2.847 656 248 084 85
1	10	1.603	-2.902 963 417 056 17
2	34	1.616	-2.903 702 732 922 11
3	77	1.584	-2.903 723 749 780 76
4	146	1.640	-2.903 724 358 396 05
5	247	1.679	-2.903 724 376 476 31
6	386	1.710	-2.903 724 377 017 38
7	569	1.751	-2.903 724 377 033 61
8	802	1.793	-2.903 724 377 034 104 549 19
9	1091	1.837	-2.903 724 377 034 119 147 20
10	1442	1.885	-2.903 724 377 034 119 584 78
11	1861	1.935	-2.903 724 377 034 119 597 90
12	2354	1.982	-2.903 724 377 034 119 598 298 933 30
13	2927	2.031	-2.903 724 377 034 119 598 310 785 54
14	3586	2.082	-2.903 724 377 034 119 598 311 146 93
15	4337	2.132	-2.903 724 377 034 119 598 311 158 66
$\psi_0^{\text{half } 2}$			
0	3	1.653	-2.890 468 719 627 22
1	14	1.660	-2.903 701 549 756 99
2	50	1.634	-2.903 724 317 102 60
3	114	1.601	-2.903 724 376 854 93
4	217	1.655	-2.903 724 377 032 07
5	368	1.682	-2.903 724 377 034 09
6	576	1.709	-2.903 724 377 034 119 229 87
7	850	1.749	-2.903 724 377 034 119 587 62
8	1199	1.793	-2.903 724 377 034 119 597 82
9	1632	1.837	-2.903 724 377 034 119 598 27
10	2158	1.885	-2.903 724 377 034 119 598 308 194 72
11	2786	1.935	-2.903 724 377 034 119 598 310 822 06
12	3525	1.982	-2.903 724 377 034 119 598 311 113 65
13	4384	2.031	-2.903 724 377 034 119 598 311 152 14
Ref. 15			-2.903 724 377 034 119 598 311 159 24

^aNumber of iteration or order.^bNumber of basis functions at order n .

particle collision area.^{3-5,7,18} We examined first the initial functions $\psi_0^{\text{log } 1}$ and $\psi_0^{\text{log } 2}$ given by Eqs. (22) and (23). The generated free ICI wave function has the form given by

$$\psi^{\text{log } 1,2} = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} (\ln s)^{j_i} (\ln u)^{k_i} \exp(-\alpha s), \quad (28)$$

where l_i runs all integers and $\{m_i, n_i\}$ run non-negative integers (m_i only even integers). From $\psi_0^{\text{log } 1}$, j_i is 0 or 1 and k_i is 0. From $\psi_0^{\text{log } 2}$, both j_i and k_i are 0 or 1. Table IV shows the results (the calculations were stopped at M_n of around 10 000). The convergent behavior was further improved in both cases of $\psi_0^{\text{log } 1}$ and $\psi_0^{\text{log } 2}$, compared with the half-integer types. Moreover, the speed of convergence did not slow down even at M_n beyond 5000. When we compare $\psi_0^{\text{log } 1}$ with $\psi_0^{\text{log } 2}$, the results with $\psi_0^{\text{log } 2}$ always show better performance than those with $\psi_0^{\text{log } 1}$ until $M_n = \sim 10\,000$. However, the speed of convergence with $\psi_0^{\text{log } 2}$ became slightly slower near $M_n = \sim 10\,000$. On the other hand, it was not so with $\psi_0^{\text{log } 1}$. The free ICI complement functions

generated from $\psi_0^{\text{log } 1}$ resemble the basis functions of Schwartz¹⁵ but different in higher-order terms. Schwartz reported the variational energy of -2.903 724 377 034 119 598 311 159 245 194 404 440 a.u. (36 digit accuracy) with 10 259 basis.¹⁵ The free ICI energy with $\psi_0^{\text{log } 2}$ at order 18 (dimension 10 794) was -2.903 724 377 034 119 598 311 159 245 194 404 34 a.u. (34 digit accuracy), which is slightly less accurate than the result of Schwartz.

C. New logarithm-type initial function

Finally, we examine our new logarithm initial function $\psi_0^{\text{new log}}$ given by Eq. (24), which was introduced to improve a flaw of $\psi_0^{\text{log } 2}$. The free ICI wave function generated from $\psi_0^{\text{new log}}$ is expressed as

$$\psi^{\text{new log}} = \sum_i c_i s^{l_i} t^{m_i} u^{n_i} [\ln(s + \beta u)]^{j_i} \exp(-\alpha s), \quad (29)$$

where l_i runs all integers, $\{m_i, n_i\}$ run non-negative integers

TABLE IV. Ground-state energies of helium atom calculated with the logarithm-type initial functions $\psi_0^{\log 1}$ and $\psi_0^{\log 2}$ given by Eqs. (22) and (23). The g function was commonly g_s^1 given by Eq. (14).

n^a	M_n^b	Optimal α	Energy (a.u.)
$\psi_0^{\log 1}$			
0	2	1.687	-2.847 656 242 128 24
1	10	1.550	-2.902 964 172 868 10
2	34	1.561	-2.903 702 734 675 68
3	77	1.619	-2.903 723 749 601 90
4	146	1.638	-2.903 724 358 395 41
5	247	1.641	-2.903 724 376 476 31
6	386	1.651	-2.903 724 377 01 739
7	569	1.670	-2.903 724 377 033 61
8	802	1.683	-2.903 724 377 034 104 549 62
9	1 091	1.696	-2.903 724 377 034 119 147 23
10	1 442	1.711	-2.903 724 377 034 119 584 79
11	1 861	1.729	-2.903 724 377 034 119 597 90
12	2 354	1.753	-2.903 724 377 034 119 598 29
13	2 927	1.779	-2.903 724 377 034 119 598 310 792 63
14	3 586	1.807	-2.903 724 377 034 119 598 311 148 17
15	4 337	1.837	-2.903 724 377 034 119 598 311 158 90
16	5 186	1.868	-2.903 724 377 034 119 598 311 159 234 996 60
17	6 139	(1.90)	-2.903 724 377 034 119 598 311 159 244 882 73
18	7 202	(1.93)	-2.903 724 377 034 119 598 311 159 245 184 83
19	8 381	(1.96)	-2.903 724 377 034 119 598 311 159 245 194 10
20	9 682	(1.99)	-2.903 724 377 034 119 598 311 159 245 194 395 277 70
$\psi_0^{\log 2}$			
0	3	1.657	-2.878 141 105 039 23
1	14	1.580	-2.903 709 499 595 37
2	50	1.595	-2.903 724 282 145 40
3	114	1.637	-2.903 724 376 535 55
4	217	1.646	-2.903 724 377 031 63
5	368	1.656	-2.903 724 377 034 10
6	576	1.653	-2.903 724 377 034 119 378 18
7	850	1.672	-2.903 724 377 034 119 595 08
8	1 199	1.683	-2.903 724 377 034 119 598 25
9	1 632	1.697	-2.903 724 377 034 119 598 310 120 79
10	2 158	1.711	-2.903 724 377 034 119 598 311 137 79
11	2 786	1.729	-2.903 724 377 034 119 598 311 158 77
12	3 525	1.753	-2.903 724 377 034 119 598 311 159 234 578 25
13	4 384	1.778	-2.903 724 377 034 119 598 311 159 244 941 21
14	5 372	1.807	-2.903 724 377 034 119 598 311 159 245 187 75
15	6 498	(1.83)	-2.903 724 377 034 119 598 311 159 245 194 18
16	7 771	(1.86)	-2.903 724 377 034 119 598 311 159 245 194 39
17	9 200	(1.89)	-2.903 724 377 034 119 598 311 159 245 194 403 517 65
18	10 794	(1.92)	-2.903 724 377 034 119 598 311 159 245 194 404 344 80
Ref.15	10 259		-2.903 724 377 034 119 598 311 159 245 194 404 440 04

^aNumber of iteration or order.^bNumber of basis functions at order n .

(m_i is even integers), and j_i is 0 or 1. Table V shows the calculated energies with the initial function $\psi_0^{\text{new log}}$ up to $n=27$ ($M_n=22\,709$). In the calculations summarized in Table V, the parameter β was fixed to $\beta=1$. Although β may be one of the variational parameters, its optimal value became small as iteration proceeded and moreover, β did not influence much the accuracy at large iteration numbers, except for the special case of $\beta=0$, in which case, i.e., $\psi_0^{\log 1}$, the results are already shown in Table IV.

As shown in Table V, the energy of Schwartz with 10 259 basis functions¹⁵ was already exceeded by our

calculations with $\psi_0^{\text{new log}}$ at order 20 with 9682 functions and at $n=27$ ($M_n=22\,709$). The free ICI energy was **-2.903 724 377 034 119 598 311 159 245 194 404 446 69690** 5 37 a.u., which is correct over 40 digits and is now the best variational energy among in published literature.²⁸

The ICI wave function starting from the new initial function including logarithm function $\ln(s+\beta u)$ is adapted to satisfy both the two- and three-particle cusp conditions that the exact SE demands. Schwartz also adopted the logarithm function and improved Kinoshita's wave function by introducing $(t/s)^m$ instead of $(t/u)^m$ (original Kinoshita type).

TABLE V. Ground-state energies of the helium atom calculated with the new logarithm-type initial function $\psi_0^{\text{new log}}$ given by Eq. (24) with $\beta=1$. The g function was g_S^1 given by Eq. (14).

n^a	M_n^b	Optimal α	Energy (a.u.)
0	2	1.827	-2.865 370 819 026 71
1	10	1.475	-2.903 536 812 281 53
2	34	1.627	-2.903 724 007 321 45
3	77	1.679	-2.903 724 375 094 16
4	146	1.683	-2.903 724 377 022 34
5	247	1.679	-2.903 724 377 034 05
6	386	1.693	-2.903 724 377 034 119 011 25
7	569	1.704	-2.903 724 377 034 119 592 84
8	802	1.707	-2.903 724 377 034 119 598 24
9	1 091	1.713	-2.903 724 377 034 119 598 309 973 48
10	1 442	1.724	-2.903 724 377 034 119 598 311 136 32
11	1 861	1.738	-2.903 724 377 034 119 598 311 158 76
12	2 354	1.757	-2.903 724 377 034 119 598 311 159 23
13	2 927	1.779	-2.903 724 377 034 119 598 311 159 244 938 53
14	3 586	1.806	-2.903 724 377 034 119 598 311 159 245 187 71
15	4 337	1.837	-2.903 724 377 034 119 598 311 159 245 194 18
16	5 186	1.866	-2.903 724 377 034 119 598 311 159 245 194 39
17	6 139	1.899	-2.903 724 377 034 119 598 311 159 245 194 403 526 60
18	7 202	(1.93)	-2.903 724 377 034 119 598 311 159 245 194 404 346 36
19	8 381	(1.96)	-2.903 724 377 034 119 598 311 159 245 194 404 433 80
20	9 682	(1.99)	-2.903 724 377 034 119 598 311 159 245 194 404 444 83
21	11 111	(2.02)	-2.903 724 377 034 119 598 311 159 245 194 404 446 40
22	12 674	(2.05)	-2.903 724 377 034 119 598 311 159 245 194 404 446 646 839 61
23	14 377	(2.08)	-2.903 724 377 034 119 598 311 159 245 194 404 446 687 685 92
24	16 226	(2.11)	-2.903 724 377 034 119 598 311 159 245 194 404 446 695 101 79
25	18 227	(2.14)	-2.903 724 377 034 119 598 311 159 245 194 404 446 696 542 44
26	20 386	(2.17)	-2.903 724 377 034 119 598 311 159 245 194 404 446 696 840 21
27	22 709	(2.20)	-2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 34
Ref. 15	10 259		-2.903 724 377 034 119 598 311 159 245 194 404 440 049 5

^aNumber of iteration or order.^bNumber of basis functions at order n .

$(t/u)^m$ brought a discontinuity (singularity) of the two-electron collision area into the wave function but $(t/s)^m$ did not. Schwartz's wave function also has good natures for the two- and three-particle cusp conditions, but is limited to the logarithm function of the form of $\ln s$. This is why the most rapid convergence was realized by using the new logarithm initial function $\psi_0^{\text{new log}}$.

D. Convergence behaviors with different functions

Here, we summarize the convergence behaviors of the different functions given above. Figure 1 shows the energy convergence behaviors of the ICI wave functions calculated from several different initial functions, i.e., normal type, half-integer type, logarithm type, and new logarithm type, given by Eqs. (19)–(24). The g function used was commonly g_S^1 of Eq. (14). Figure 1 is the plots of the following Δ :

$$\Delta = -\log_{10}(E - E_0), \quad (30)$$

against the number of the complement functions at different orders (iterations) of the different free ICI calculations. In the above equation, E is the energy at that stage and E_0 is the best energy correct at least to 40 digits obtained with the initial function $\psi_0^{\text{new log}}$ at iteration 27 (dimension of 22 709).

So, Δ represents the number of the correct digits of the calculated energy.

As Fig. 1 shows, all calculations monotonically converge to the exact energy from above. For getting chemical and spectroscopic accuracies ($\Delta=3-6$), any choice of ψ_0 is okay. The convergence of the free ICI is quite nice. However, when one desires much higher accuracy, the speed of the convergence is quite different, depending on the choice of ψ_0 . The performance with the normal type ψ_0 is good until 1000 dimensions but becomes very slow after then. The half-integer type is successful in improving the convergence behavior. However, it also slows down after 3000 or 4000 dimensions, indicating that the half-integer-type initial function is also unsatisfactory for quite accurate calculations. The performance of the free ICI in this highly accurate region is greatly improved by using the logarithm-type initial function. This is clearly due to the effective correct description of the wave function in the three-particle coalescence region.

In the present article, we introduced the logarithm initial functions $\psi_0^{\log 2}$ and $\psi_0^{\text{new log}}$ including both $s=r_1+r_2$ and $u=r_{12}$. Both calculations with $\psi_0^{\log 2}$ and $\psi_0^{\text{new log}}$ showed quite good performance but the convergence speed with $\psi_0^{\log 2}$ slowed down after 8000 dimensions, indicating that the $\ln u$

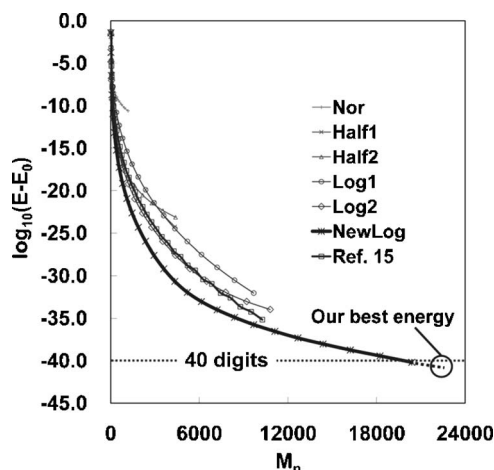


FIG. 1. Convergence behavior of the free ICI calculations with several initial functions given by Eqs. (19)–(21), (23), and (24). The g function was commonly g_S^1 given by Eq. (14).

term is not so important for the energy beyond 35 digit accuracy. In contrast, the calculations with the initial function $\psi_0^{\text{new log}}$ continued to show very good performance even beyond 10 000 dimensions (35 digit accuracy). Figure 1 also shows the plot of the energies Schwartz reported in his paper.¹⁵ Since he also used the logarithm function in his basis set, the convergence behavior was so good until 10 000 dimensions. The fastest convergence (at least until 10 000 dimensions) was seen in Fig. 1 for the calculations with $\psi_0^{\text{new log}}$. For example, comparing our result at iteration 17 (dimensions of 6139) with Schwartz's one at dimension of 6255, our result is about three digits better than his. However, in the range exceeding 10 000 dimensions, both of our calculations with $\psi_0^{\text{new log}}$ and $\psi_0^{\text{log } 1}$ and Schwartz's calculations show slightly slower convergence. One possible reason would be the usage of only first-order logarithm function in the initial function. Actually, the originally proposed logarithm function included all orders of the logarithm term,^{3–5} $(\ln[(s^2 + t^2)^{1/2}])^j$ ($j=0, 1, 2, \dots$), but we included only the first-order term. Another reason may be the usage of only a single exponent function. Although the logarithm singularity improves very short-range correlation, our wave function does not include the functions adequate for describing the

very outer region of the atom. To improve this region, we might have to include more flexible multiple- ζ functions.

In the free ICI method, the choice of the initial function ψ_0 is very important since it determines the functional form of the complement functions of the free ICI wave function. The experience accumulated in the present calculations of the accurate wave functions of helium atom seems to show that the inclusion of the functions that reflect the physics of the system in the initial function ψ_0 greatly improves the convergence speed to the exact solution of the SE.

E. Helium isoelectronic ions

Finally, we apply the best free ICI scheme established above to the calculations of accurate wave functions and energies of the helium isoelectronic ions from $Z=1$ (H^-) to $Z=10$ (Ne^{8+}). We use g_S^1 and $\psi_0^{\text{new log}}$ given by Eqs. (14) and (24), respectively, as the best combination. The calculations were stopped at $n=20$ (dimension of 9682) except for the neutral helium atom explained above ($n=27$ and dimension of 22 709). We note that at the same order (iteration), the free ICI wave functions of all isoelectronic atoms have the same functional form. All the complement functions are the same. After variational optimizations of the parameters contained, each wave function gains each unique character as each atom. The nonlinear parameter α in the initial function $\psi_0^{\text{new log}}$ was fixed to the guess optimal value, $\alpha=0.4$ for $Z=1$, $\alpha=2.2$ for $Z=2$, and $\alpha=1.3Z-0.7$ for $Z=3-10$. The parameter β was fixed to unity.

Table VI shows the summary of the calculated energies. For helium, the result is for $n=27$ and the result for $n=20$ is seen in Table V. Recently, Frolov²⁹ reported highly accurate variational calculations for H^- ($Z=1$) using a large number of Slater geminal functions and reported the most accurate energy of $-0.527\,751\,016\,544\,377\,196\,589\,759$ a.u. with 3700 basis functions including so many nonlinear parameters. In the present ICI calculations, we obtained the variational energy of $-0.527\,751\,016\,544\,377\,196\,590\,813$ a.u. at order 14 with 3586 functions, which already exceeded Frolov's energy with a smaller number of functions than that of Frolov. We continued the calculations until $n=20$ and obtained the energy of

TABLE VI. Energies of the helium atom and its isoelectronic ions ($Z=1-10$) calculated with $\psi_0^{\text{new log}}$ given by Eq. (24) with $\beta=1$ and g_S^1 given by Eq. (14). All calculations were stopped at $n=20$ (dimension 9682) except for the helium atom for which $n=27$ (dimension of 22 709).

Z	Atom	Optimal α	Energy (a.u.)
1	H^-	(0.4)	$-0.527\,751\,016\,544\,377\,196\,590\,814\,566\,747\,511\,383\,045\,02$
2	He	(2.20)	$-2.903\,724\,377\,034\,119\,598\,311\,159\,245\,194\,404\,446\,696\,905\,37$
3	Li^+	(3.2)	$-7.279\,913\,412\,669\,305\,964\,919\,459\,221\,006\,611\,682\,572\,35$
4	Be^{2+}	(4.5)	$-13.655\,566\,238\,423\,586\,702\,081\,730\,194\,612\,159\,391\,360\,60$
5	B^{3+}	(5.8)	$-22.030\,971\,580\,242\,781\,541\,655\,702\,043\,566\,870\,379\,775\,99$
6	C^{4+}	(7.1)	$-32.406\,246\,601\,898\,530\,310\,557\,357\,969\,530\,254\,566\,016\,97$
7	N^{5+}	(8.4)	$-44.781\,445\,148\,772\,704\,645\,185\,760\,848\,954\,056\,776\,028\,12$
8	O^{6+}	(9.7)	$-59.156\,595\,122\,757\,925\,558\,549\,892\,445\,559\,527\,700\,907\,85$
9	F^{7+}	(11.0)	$-75.531\,712\,363\,959\,491\,104\,878\,015\,579\,533\,576\,560\,909\,77$
10	Ne^{8+}	(12.3)	$-93.906\,806\,515\,037\,549\,421\,469\,184\,180\,000\,241\,066\,651\,70$

– **0.527 751 016 544 377 196 590 814 566 747 511** 383 045 02 a.u., which is the world's best variational energy of H^- at this moment. For the other isoelectronic ions ($Z=3-10$), we were also able to obtain the best variational energies.

Sims and Hagstrom¹² calculated Li^+ , Be^{2+} , and B^{3+} with the Hylleraas-CI method and obtained the energies of **–7.279 913 412 669 305 964 899**, **–13.655 566 238 423 586 702 06**, and **–22.030 971 580 242 781 541 63** a.u. with 4284, 4648, and 4648 functions, respectively. In comparison, we obtained the energies of Li^+ , Be^{2+} and B^{3+} as **–7.279 913 412 669 305 964 918**, **–13.655 566 238 423 586 702 080**, and **–22.030 971 580 242 781 541 653** a.u., respectively, at order 9 with 1091 functions. The free ICI results seem to be better than those of Sims and Hagstrom with a smaller number of functions.

The new logarithm-type initial functions are proven to show very good performance for ions ($Z=3-10$) as well as for the neutral helium atom ($Z=2$). For H^- ($Z=1$), however, the logarithm function did not so drastically improve the convergent behavior, because H^- is an anion and physically, the three-particle collision is not so important.

Finally, a rough technical note on a computer time is given, though our program is far from being tuned up on the computational speed. The timing was done for the results given in Table VI at $n=20$ and $M_n=9682$ starting with g_S^1 and $\psi_0^{new\log}$. As described in the last paragraph of Sec. III, our program consists of the three steps and the first step (generating the complement functions of free ICI), second step (integrations), and final step (diagonalization) took about 3 h, 2 days, and 1.5 days, respectively, with a single Intel(R) Core2 Duo 2.8 GHz workstation. We used MAPLE in the second step, which means that this step can be substantially accelerated. Anyway, roughly 4 days are enough to get the world's best energy and analytical wave function of the helium isoelectronic ions.

V. CONCLUSION

In the history of accurate calculations of He atom, starting from the pioneering work of Hylleraas just three years after the birth of quantum mechanics, a lot of effort has been done to describe the wave function of this atom as accurately as possible. These were done mostly with intuition, using, for example, the necessary conditions that the exact wave function must satisfy, such as the two-particle and three-particle cusp conditions, etc., since there was no general theory for constructing the exact wave function of the SE. This approach was quite successful as proven from the monumental work of Schwartz. However, their experiences were difficult to generalize for solving the SE of general atoms and molecules.

In contrast to these studies, we performed the calculations based on the general theory of solving the SE in an analytical expansion form recently developed in our laboratory. Starting from the cleverly chosen ψ_0 and using the effective g function, we can automatically generate, by free ICI method, a series of functions (called complement functions)

that are guaranteed to construct the exact wave function when the order n is enough. By determining the parameters involved by the variational method, we could obtain the world's best results of helium and its isoelectronic ions. The present results indicate that by continuing the free ICI calculations systematically, we would be able to solve the SE to any desired accuracy.

We examined several different types of g and initial function ψ_0 . The chemical and spectroscopic accuracies were easily achieved at a few iterations with the use of any set of these functions. However, to achieve extremely high accuracy, it was important to select these sets cleverly based on the physical insight. The sum-type g function showed better performance than the product-type one because the former generates more flexible functions than the latter. It was also very important to select ψ_0 cleverly because it is the zeroth order wave function from which the Hamiltonian of the system constructs its own complement functions following the principle of the free ICI theory. The logarithm initial functions, in particular, the new logarithm function $\ln(s+\beta u)$, showed quite good performance, admitting some necessary conditions of the SE such as two-particle and three-particle cusp conditions. Actually, compared with the other calculations, the most rapid convergence was obtained by the free ICI method with the new logarithmic initial function at least until 10 000. Using this initial function, we calculated the free ICI wave functions of helium and its isoelectronic ions and obtained the world's best results in the published literature. It is interesting to note that the free ICI wave functions of helium and its isoelectronic ions consisted of the same complement functions when the order n is the same, except for the values of the parameters, α , etc., involved. This is generally true for the wave functions of a series of atoms having the same number of electrons as long as the initial function and the scaling function are the same.

The experience obtained here for accurate calculations of helium and its isoelectronic ions may be generalized in the free ICI calculations of more general atoms and molecules. The free ICI method itself and the algorithm of the calculations are not limited to the helium atom alone but they are applicable and extendable to general atoms and molecules. Actually, we used the same method for calculations of accurate wave functions of hydrogen molecule²³ and three to five electron atoms.³⁰ For more general atoms and molecules, however, analytic integrations over the free ICI complement functions would become difficult. For such cases, we have developed a method, called local Schrödinger equation method and applied it successfully to several atoms and molecules. These results will be published elsewhere in the literature.²⁵

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APPENDIX: FORMULATIONS FOR THE INTEGRALS INCLUDING LOGARITHM FUNCTIONS

We briefly summarize the analytical calculations of several integrals for variational calculations of the ICI wave function starting from the new logarithm function including $\ln(s+\beta u)$ and $\ln u$. The formulations are quite simple. The integrals we want to calculate are written as

$$I_{p,q}(a,b,c,d;\alpha,\beta) = \int_0^\infty ds \cdot s^a (\ln s)^p \exp(-\alpha s) \\ \times \int_0^s du \cdot u^b \frac{(\ln(s+\beta u))^q}{(s+\beta u)^d} \int_0^u dt \cdot t^c, \quad (\text{A1})$$

$$J_{p,q}(a,b,c;\alpha) = \int_0^\infty ds \cdot s^a (\ln s)^p \exp(-\alpha s) \\ \times \int_0^s du \cdot u^b (\ln u)^q \int_0^u dt \cdot t^c, \quad (\text{A2})$$

where the indices a, b, c, d, p , and q run integer values; p and q of the logarithm terms were limited to 0, 1, and 2 in the present paper. α and β are nonlinear parameters, whose ranges are $\alpha > 0$ and $\beta > -1$, respectively.

First, we define basic one-dimensional integral of the s coordinate as

$$F_p(n;\alpha) = \int_0^\infty ds \cdot s^n (\ln s)^p \exp(-\alpha s). \quad (\text{A3})$$

The general formula of this integral is well known and can be found in some mathematical books.

We want to calculate the integral $I_{p,q}$ defined in Eq. (A1). The basic strategy is to reduce the integral $I_{p,q}$ to the one-dimensional basic integral F_p defined in Eq. (A3) by performing partial integrations on the u coordinate. Considering the numerical estimation of the integral by programming, we group the cases by the indices as follows.

(i) $q=0, d=0$. In this case, since the integral $I_{p,q}$ does not include any $s+\beta u$ term, the integration is simplified as

$$I_{p,0}(a,b,c,0;\alpha,\beta) = \frac{1}{(c+1)(b+c+2)} \\ \times F_p(a+b+c+2;\alpha). \quad (\text{A4})$$

(ii) $q=1, d=0$. In this case, the integral $I_{p,q}$ includes the $\ln(s+\beta u)$ term. The integration by parts is successively performed on the u coordinate and we can reduce $I_{p,q}$ to the one-dimensional integral of the s coordinate expressed as

$$I_{p,1}(a,b,c,0;\alpha,\beta) = \frac{1}{c+1} \{ a_1^\beta (b+c+1) \\ \cdot F_{p+1}(a+b+c+2;\alpha) \\ + a_0^\beta (b+c+1) \cdot F_p(a+b+c+2;\alpha) \}, \quad (\text{A5})$$

where $a_1^\beta(n)$ and $a_0^\beta(n)$ are the coefficients depending on n and β , written as

$$a_1^\beta(n) = \frac{1}{n+1}, \quad (\text{A6})$$

$$a_0^\beta(n) = \frac{\ln(\beta+1)}{n+1} \left(1 - \frac{(-1)^{n+1}}{\beta^{n+1}} \right) + \frac{1}{n+1} \sum_{k=1}^{n+1} \frac{(-1)^{n-k+2}}{\beta^{n+1-k}} \frac{1}{k}. \quad (\text{A7})$$

(iii) $q=2, d=0$. Similarly to the above case, after successively performing partial integrations on the u coordinate, we get

$$I_{p,2}(a,b,c,0;\alpha,\beta) = \frac{1}{c+1} \{ b_2^\beta (b+c+1) \\ \cdot F_{p+2}(a+b+c+2;\alpha) \\ + b_1^\beta (b+c+1) \\ \cdot F_{p+1}(a+b+c+2;\alpha) \\ + b_0^\beta (b+c+1) \cdot F_p(a+b+c+2;\alpha) \}, \quad (\text{A8})$$

where $b_2^\beta(n)$, $b_1^\beta(n)$, and $b_0^\beta(n)$ are the coefficients expressed as

$$b_2^\beta(n) = \frac{1}{n+1} = a_1^\beta(n), \quad (\text{A9})$$

$$b_1^\beta(n) = \frac{2 \ln(\beta+1)}{n+1} \left(1 - \frac{(-1)^{n+1}}{\beta^{n+1}} \right) \\ + \frac{2}{n+1} \sum_{k=1}^{n+1} \frac{(-1)^{n-k+2}}{\beta^{n+1-k}} \frac{1}{k} = 2a_0^\beta(n), \quad (\text{A10})$$

$$b_0^\beta(n) = \frac{(\ln(\beta+1))^2}{n+1} \left(1 - \frac{(-1)^{n+1}}{\beta^{n+1}} \right) - 2a_0^\beta(n) \\ + \frac{2}{n+1} \sum_{k=1}^n \left\{ \frac{(-1)^{n-k}}{\beta^{n-k}} \left(a_0^\beta(k) + \frac{a_0^\beta(k-1)}{\beta} \right) \right\}. \quad (\text{A11})$$

(iv) $q=0, d \geq 1$. Similarly to the above, we can get

$$I_{p,0}(a,b,c,d;\alpha,\beta) = \frac{1}{c+1} \{ c_0^\beta (d,b+c+1) \\ \cdot F_p(a+b+c-d+2;\alpha) \}, \quad (\text{A12})$$

where the coefficient $c_0^\beta(d,n)$ is written case by case. For $n < d$, $d=n+1$, $c_0^\beta(d,n)$ is written as

$$c_0^\beta(n+1,n) = \frac{-1}{(\beta+1)^{n+1}} \sum_{k=1}^n \frac{(\beta+1)^k}{\beta^k(n-k+1)} + \frac{\ln(\beta+1)}{\beta^{n+1}}, \quad (\text{A13})$$

and for $n < d$, $d \neq n+1$, $c_0^\beta(d,n)$ is written as

$$c_0^\beta(d, n) = \sum_{k=1}^{n+1} \frac{(-1)^{k+1}}{\beta^k(\beta+1)^{d-k}} \frac{\prod_{i=0}^{k-2}(n-i)}{\prod_{i=0}^{k-1}(1-d+i)} + \frac{(-1)^{n+1} \prod_{i=0}^{n-1}(n-i)}{\beta^{n+1} \prod_{i=0}^n(1-d+i)}, \quad (\text{A14})$$

and for $n \geq d$,

$$c_0^\beta(d, n) = \sum_{k=1}^{d-1} \frac{(-1)^{k+1}}{\beta^k(\beta+1)^{d-k}} \frac{\prod_{i=0}^{k-2}(n-i)}{\prod_{i=0}^{k-1}(1-d+i)} + \frac{(-1)^{d-1} \prod_{i=0}^{d-2}(n-i)}{\beta^{d-1} \prod_{i=0}^{d-2}(1-d+i)} \left\{ \frac{\ln(\beta+1)}{\beta} - \frac{n-d+1}{\beta} a_0^\beta(n-d) \right\}. \quad (\text{A15})$$

(v) $q=1$, $d \geq 1$. Similarly, we get

$$I_{p,1}(a, b, c, d; \alpha, \beta) = \frac{1}{c+1} \{ d_1^\beta(d, b+c+1) \cdot F_{p+1}(a+b+c-d+2; \alpha) + d_0^\beta(d, b+c+1) \cdot F_p(a+b+c-d+2; \alpha) \}, \quad (\text{A16})$$

where the coefficient $d_1^\beta(d, n)$ and $d_0^\beta(d, n)$ are also written case by case as follows. For $n < d$, $d=n+1$,

$$d_1^\beta(n+1, n) = - \sum_{k=1}^n \frac{(\beta+1)^{k-n-1}}{\beta^k(n-k+1)} + \frac{\ln(\beta+1)}{\beta^{n+1}}, \quad (\text{A17})$$

$$d_0^\beta(n+1, n) = - \sum_{k=1}^n \frac{(\beta+1)^{k-n-1}}{\beta^k(n-k+1)} \left\{ \frac{1}{n-k+1} + \ln(\beta+1) \right\} + \frac{(\ln(\beta+1))^2}{2\beta^{n+1}} + \sum_{k=1}^n \frac{c_0^\beta(n-k+1, n-k)}{\beta^k(n-k+1)}, \quad (\text{A18})$$

for $n < d$, $d \neq n+1$,

$$d_1^\beta(d, n) = - \sum_{k=1}^n \frac{(\beta+1)^{k-d} \prod_{i=1}^{k-1}(n-i+1)}{\beta^k \prod_{i=1}^k(d-i)} + \frac{\prod_{i=1}^n(n-i+1)}{\beta^{n+1} \prod_{i=1}^{n+1}(d-i)} \{1 - (\beta+1)^{n-d+1}\}, \quad (\text{A19})$$

$$d_0^\beta(d, n) = - \sum_{k=1}^n \frac{(\beta+1)^{k-d} \prod_{i=1}^{k-1}(n-i+1)}{\beta^k \prod_{i=1}^k(d-i)} \left\{ \frac{1}{d-k} + \ln(\beta+1) - \frac{n-k+1}{d-k} c_0^\beta(d-k, n-k) \right\} + \frac{\prod_{i=1}^n(n-i+1)}{\beta^{n+1} \prod_{i=1}^{n+1}(d-i)} \left[\frac{1}{d-n-1} \{1 - (\beta+1)^{n-d+1}\} - (\beta+1)^{n-d+1} \ln(\beta+1) \right], \quad (\text{A20})$$

and for $n \geq d$,

$$d_1^\beta(d, n) = - \sum_{k=1}^{d-1} \frac{(\beta+1)^{k-d} \prod_{i=1}^{k-1}(n-i+1)}{\beta^k \prod_{i=1}^k(d-i)} + \frac{\prod_{i=1}^{d-1}(n-i+1)}{\beta^d \prod_{i=1}^{d-1}(d-i)} \left\{ \ln(\beta+1) - \frac{n-d+1}{2} b_1^\beta(n-d) \right\}, \quad (\text{A21})$$

$$d_0^\beta(d, n) = - \sum_{k=1}^{d-1} \frac{(\beta+1)^{k-d} \prod_{i=1}^{k-1}(n-i+1)}{\beta^k \prod_{i=1}^k(d-i)} \left\{ \frac{1}{d-k} + \ln(\beta+1) - \frac{n-k+1}{d-k} c_0^\beta(d-k, n-k) \right\} + \frac{\prod_{i=1}^{d-1}(n-i+1)}{2\beta^d \prod_{i=1}^{d-1}(d-i)} \{(\ln(\beta+1))^2 - (n-d+1)b_0^\beta(n-d)\}. \quad (\text{A22})$$

Finally, we have to calculate the integral $J_{p,q}$ defined by Eq. (A2). We again perform successive partial integrations on the u coordinate, we can get

$$J_{p,q}(a, b, c; \alpha) = \frac{1}{c+1} \sum_{k=0}^q \frac{(-1)^{q-k} \prod_{i=0}^{q-k-1}(q-i)}{(b+c+2)^{q-k+1}} F_{p+k}(a+b+c+2; \alpha). \quad (\text{A23})$$

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